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THE GENERAL PRINCIPLES UNDERLYING METAMORPHIC PROCESSES

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PART II

THE PHASE RULE

The phase rule, which recently has been applied to metamorphic rocks,[1] orients us as to the number of phases which, for a given number of components and for given external conditions, can be in equilibrium with one another. According to the phase rule $f=c-n+2$, where f, c, and n are the number of degrees of freedom, of components, and of phases, respectively.[2] If f is zero, the system is stable only when temperature, pressure, and concentration (composition) of each phase have definite and singular values. If f is 1, a change of one of the above three parameters induces definite and definitely related alterations of the other two, if the number and nature of the phases is to remain unaltered. If f is 2, any two of the above parameters may be changed; such a system can exist at any pressure or temperature within certain limits, although under such circumstances the composition of all the phases present is at any moment definitely fixed. Thus a system with two degrees of freedom can in general exist throughout a range of temperatures and pressures; if the system actually had only one degree of freedom, it could only be accidental if the corresponding values were chosen. Therefore the number of possible phases coexisting *in equilibrium* during metamorphic processes will in general not be greater than the number of components. The essentials of the phase rule and their application to simple systems are so readily understood that there is always a temptation to neglect their specific limitations; limitations which are especially prominent when, as in the case of metamorphic processes, we endeavor to reason backward from the end-result of the process.

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[1] V. M. Goldschmidt, *Kontaktmetamorphose im Kristiania-Gebiet*, Kristiania, 1911, and in other papers; P. Niggli, "Chloritoidschiefer des nordöstlichen Gotthardmassives," *Beiträge geol. Karte Schweiz*, N. F., XXXVI (1912).

[2] "A heterogeneous system is made up of different portions, each in itself homogeneous, but marked off in space and separated from the other portions by bounding surfaces; these homogeneous, physically distinct, and mechanically separable portions are called *phases*" (Findlay, *Phase Rule*, p. 9).

"As the *components* of a system there are to be chosen the *smallest number* of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation" (*ibid.*, p. 12).

"The number of degrees of freedom of a system is the number of the variable factors, temperature, pressure, and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined" (*ibid.*, p. 15).

For a full discussion of these matters the reader is referred to Findlay's book.

Limitations to the applicability of the phase rule to metamorphic systems.—Application of the phase rule presupposes that the pressure (and temperature) is uniform throughout the system[1]. Now it is clear that absolutely uniform pressure (or temperature) can never occur during rock metamorphism; we may have anything from great inequality in the stresses in the three principal directions to a nearly equal distribution of the three stresses. On the relative and absolute magnitude of the variation of the resultant stress from point to point depends its influence on the result. If the particular paragenetic transformation can still go on in spite of considerable variations of either temperature or pressure from the mean values which actually obtain, it will not be much affected by the local stress variation; if otherwise, great local variation of results may be expected. Moreover, similarly variable results will be produced by the changes of temperature and pressure which accompany the process of metamorphism.

Reference to the discussion of phases and components given in the textbooks renders it evident that great caution must be exercised in guessing (inferring) the actual components from an examination of the more or less ultimate state of any given rock. It is an essential property of a component that it is always in reaction with the other members of the system throughout the establishment of equilibrium. But the fact that under laboratory conditions a component is so insoluble that its rate of reaction seems so small as to be negligible does not prove that in geological phenomena, for which unlimited time is available, the influence of such a component can be neglected. Moreover, the similarity in chemical nature of certain oxides does not justify grouping them together as a single component, in an effort to simplify the system under consideration; for the behavior of the numerous two-component systems hitherto studied shows that the grouping-together of the oxides of the alkalies, or of the alkaline earths, or of alumina and iron, is of doubtful validity.

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[1] Further, that there are (*inter alia*) no surface effects; this condition might be unfulfilled in certain cases, e.g., with very porous rock-masses.

By means of the microscope it is often possible to distinguish between original and new components. The presence of any original components which could not have been formed by the metamorphic process indicates that the forces were not intense enough, or did not last long enough, to render the alteration complete; we have then an incompletely metamorphosed rock. On the other hand, the presence of original quartz grains alongside new quartz (as is frequently observed) is no proof of incomplete metamorphism, because quartz, which is stable throughout a very wide range of conditions, may appear in spite of considerable variation of chemical composition, temperature, or pressure. Again, it is a question of the stability of the new forms. When one recalls how frequently metastable forms appear in laboratory work and considers the special circumstances of metamorphism, one need not be surprised if metastable substances occur frequently in nature also even though the conditions of formation remain undisturbed for long periods of time. Metastable forms are observed oftenest with polymorphic or hydrated substances; their occurrence therefore in general changes only the nature, but not the number of the phases present. For instance, so far as the phase rule is concerned, it does not matter though kyanite appear instead of the stable sillimanite.[1]

Metamorphic processes are merely the result of a tendency toward a new equilibrium position; whether this new position of equilibrium is reached or not, depends, however, on a number of factors. It is a question if a rock as a whole can always be considered as a single system, within which complete mutual actions and reactions are possible. This may well be so if the original rock was fairly homogeneous and not too coarse grained. In the case of rocks the solubility of most of the substances concerned is so small that contact with a small amount of material can suffice for the production of saturated solutions; and so the new material will be the same throughout such a system, although the amount of material in solution at any moment is small. But whether all of the original components, which by reason of the changed conditions have become unstable, disappear or not depends upon the rate of reaction, upon the time, and upon the presence of catalytic agencies; furthermore, if any of the components or intermediate or reaction-products are present as grains of appreciable size, they may become coated with some stable substance and hence—owing to the slowness (and even absence) of diffusion in the solid state—be protected against further action.

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[1] The *simultaneous* occurrence of both sillimanite and kyanite would of course increase the number of phases by one.

When to these circumstances which hinder the attainment of equilibrium we add the complications introduced by phenomena such as resorption,[1] the occurrence of reactions in the solid state (including monotropic and enantiotropic changes) and the existence of compounds which, while unstable on fusion, are able to form at lower temperatures; further, when we consider that some of the essential components may by reason of their volatility have escaped from the system and that the influence of pressure upon stability relations is practically unknown—when we remember this formidable array of possibilities, we should hardly expect to draw immediate or final conclusions merely through application of the phase rule in such complicated polycomponent systems as rocks.

Consequently, the phase rule cannot always be expected to hold rigidly or to serve in any manner as an "open sesame" in such studies. What we observe is that there appear, for a given metamorphic process and for a given number of components, only a limited number out of all the possible compounds; moreover, that the number of definite and important minerals formed by a metamorphic process usually does not exceed the maximum number

[1] For an example, see p. 593.

postulated by the phase rule. On the other hand, while in several cases the number of phases found does not exceed the number predicted from a consideration of the phase rule, on the specific assumptions that equilibrium has been reached and that the components have been correctly inferred, yet the presence of more or fewer phases than expected proves nothing except that the assumptions were wrong.

From the discussion of these limitations to the phase rule we conclude, therefore, that our present knowledge of the facts concerned is so scanty that the phase rule is not yet of much service in aiding us to describe the natural history of metamorphic rocks.[1] Nevertheless it may be of assistance in the classification of rocks; for this reason, and in order to emphasize by means of actual illustrations some of the statements made in the above paragraphs, we include a brief discussion of the application of the phase rule to ternary systems.

The ternary system—lime-alumina-silica.—The relative simplicity of two-component systems tempts one to assume that systems of three or more components may somehow be considered in an equally simple manner. That such is not the case is amply demonstrated by the lime-alumina-silica series, which has recently been very thoroughly investigated[2] at constant pressure.

From this work, in which the variables considered are only concentration and temperature, it follows that there are—instead of the simple ternary relation with a single ternary eutectic, such as the textbooks commonly treat—about eighteen invariant points (at which 3 solid phases coexist with 1 liquid phase) any one of which might under proper conditions show the usual eutectic properties (e.g., eutectic structure).[3]

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[1] The phase rule will of course be an indispensable adjunct when the experimental facts are available.

[2] E. S. Shepherd and G. A. Rankin, "Preliminary Report on the Ternary System $CaO-Al_2O_3-SiO_2$," *Jour. Ind. Eng. Chem.*, III (1911), 211; *Z. anorg. Chem.*, LXXI (1911), 19.

[3] In passing it may be suggested that the so-called eutectic structure as inferred from the study of alloys may or may not occur in the case of silicates. It is readily conceivable that systems in no sense eutectic may easily yield the so-called eutectic structure and vice versa; cf. Shepherd and Rankin, *loc. cit.*

The provisional diagram given by Shepherd and Rankin is reproduced in Fig. 1; we shall make no attempt to discuss it here, except in regard to two points, viz., (1) the occurrence of resorption, and (2) the formation of very different end-products from systems of very similar original composition.

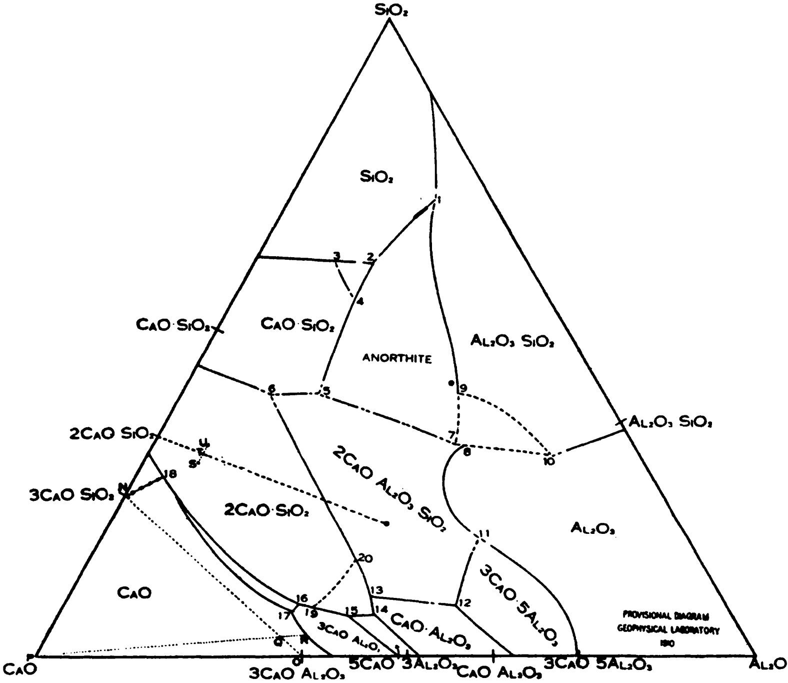

FIG. 1.—Provisional Diagram[1] for System CaO · Al_2O_3 · SiO_2

Consider a mixture the composition of which is represented by a point on the line *PQ*, and suppose it to be cooling. Lime crystals separate, the composition of the melt moves along the line *PQR* until the point *R* on the boundary curve *R*–17 is reached. At this point the solid phase ($3CaO \cdot Al_2O_3$) begins to separate, which is possible only by resorption of CaO; the composition of the melt moves along the boundary curve *R*–17 until the invariant point 17 is reached, when the whole solidifies to the three phases (CaO), ($3CaO \cdot Al_2O_3$), and ($3CaO \cdot SiO_2$). In this case only part of the free CaO is resorbed; but if the original composition had been represented by a point on the line *QR* (i.e., outside the triangle *NOP*) the CaO would be completely resorbed, the final crystallization occurring at invariant point 15, at which the phases ($3CaO \cdot Al_2O_3$), ($5CaO \cdot 3Al_2O_3$), and ($2CaO \cdot SiO_2$) are in equilibrium. All of these phenomena occur, be it noted, without interruption of the normal cooling or the intervention of any external disturbing factor.

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[1] The position of several of the points which were still doubtful at the time this diagram was published has now been more definitely established by further investigation, the results of which will appear in a forthcoming paper by Rankin. These changes, however, do not affect any of the deductions which appear in the paper of Shepherd and Rankin (*loc. cit.*).

As regards the second point, consider compositions along the line *STU*, the total length of which corresponds to a change of only 3 per cent in the amount of CaO present. Compositions on the line *ST* solidify at invariant point 16, 15, or 14, according to the original position on the line; the ternary grouping formed is either ($3CaO \cdot SiO_2$), ($2CaO \cdot SiO_2$), ($3CaO \cdot Al_2O_3$), or ($5CaO \cdot 3Al_2O_3$), ($3CaO \cdot Al_2O_3$), ($2CaO \cdot SiO_2$), or ($5CaO \cdot 3Al_2O_3$), ($2CaO \cdot SiO_2$), ($CaO \cdot Al_2O_3$). Compositions on the line *TU* solidify at point 6, forming the grouping ($2CaO \cdot SiO_2$), ($CaO \cdot SiO_2$), ($2CaO \cdot Al_2O_3 \cdot SiO_2$); while the compositions corresponding to *T* (or any point on the line joining the compositions $2CaO \cdot SiO_2$, $2CaO \cdot Al_2O_3 \cdot SiO_2$) behave as binary systems, solidifying to the two phases ($2CaO \cdot SiO_2$), ($2CaO \cdot Al_2O_3 \cdot SiO_2$).

These facts—and indeed the general appearance of the diagram—illustrate the complications likely to be encountered in relatively simple systems, and show that for systems of from four to eight or more components appearances afford a plain warning against hasty generalization, even if initial homogeneity of material and the continuous attainment of equilibrium could be assumed.

The ternary system $CaCl_2$-$MgCl_2$-H_2O.—This system, which was very carefully investigated by Van't Hoff, Kendrick, and Dawson,[1] is an example of a system with a variable phase (solution). The determination of the quintuple point of such a system will always be a matter of great difficulty, since in this case pressure, temperature and concentration (composition of the variable phase) are all fixed.

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[1] *Z. physik. Chem.*, XXXIX (1902), 27.

At 1 atm. and 21°95 there is equilibrium between the four phases ($MgCl_2 \cdot 6H_2O$), ($CaCl_2 \cdot 6H_2O$), ($CaCl_2$, $2MgCl_2$, $12H_2O$),[1] and solution, the composition of which is $100H_2O$, $4.92MgCl_2$, $9.27CaCl_2$. The reaction may therefore be written as follows:

$$\underset{\substack{\text{Solid}\\ A}}{1\,(MgCl_2\cdot 6H_2O)} + \underset{\substack{\text{Solid}\\ C}}{1.188\,(CaCl_2\cdot 6H_2O)} = \underset{\substack{\text{Solid}\\ B}}{0.252\,(CaCl_2\cdot 2MgCl_2\cdot 12H_2O)} + \underset{\substack{\text{Solution}\\ L}}{0.101\,(100H_2O,\ 4.92MgCl_2,\ 9.27CaCl_2)}$$

Now if the temperature is changed, the pressure remaining constant, one of the above 4 phases must disappear; and it has been found that the right-hand side is favored by increase of temperature. Therefore at temperatures below 21°95 and 1 atm. there can coexist: either

$$(MgCl_2\cdot 6H_2O),\ (CaCl_2\cdot 6H_2O),\ \text{solution} \qquad (\text{I})$$

or

$$(MgCl_2\cdot 6H_2O),\ (CaCl_2\cdot 6H_2O),\ (CaCl_2\cdot 2MgCl_2\cdot 12H_2O) \qquad (\text{II})$$

while at higher temperatures the possible stable configurations are either

$$(CaCl_2\cdot 2MgCl_2\cdot 12H_2O),\ \text{solution},\ (CaCl_2\cdot 6H_2O) \qquad (\text{III})$$

or

$$(CaCl_2\cdot 2MgCl_2\cdot 12H_2O),\ \text{solution},\ (MgCl_2\cdot 6H_2O) \qquad (\text{IV})$$

The solution has a definite composition corresponding to each temperature. For instance, at 16°7 in contact with ($MgCl_2 \cdot 6H_2O$) and ($CaCl_2 . 6H_2O$) its composition is $100H_2O$, $6.69CaCl_2$, $5.94 MgCl_2$; while at 28°2, in contact with ($CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$) and ($MgCl_2 \cdot 6H_2O$), it is $100H_2O$, $8.84CaCl_2$, $5.37MgCl_2$.

From this it is evident that not all the systems whose composition can be expressed in terms of $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$ and H_2O can give the 3-phase combinations I, II below 21°95, or III, IV at temperatures above 21°95. This may be illustrated by the isotherm for 23° (and 1 atm.), which has the general form given in Fig. 2. *PQ* is the solubility curve of *A*, *QR* that of *B* (tachhydrite), and *RS* that of *C*. The point *Q* gives the composition of the solution in equilibrium at 23° with *A* and *B; R*, of that in equilibrium with *B* and *C*. The combination (*A B*, solution *Q*) can result only when the gross composition is within the triangle *ABQ;* the combination (*B C*, solution *R*), only when the composition falls within *BCR*. The triangles *APQ*, *BQR*, and *CRS* are the regions in which the two-phase combinations of solutions with *A*, *B*, or *C*, respectively, are stable.

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[1] The so-called tachhydrite.

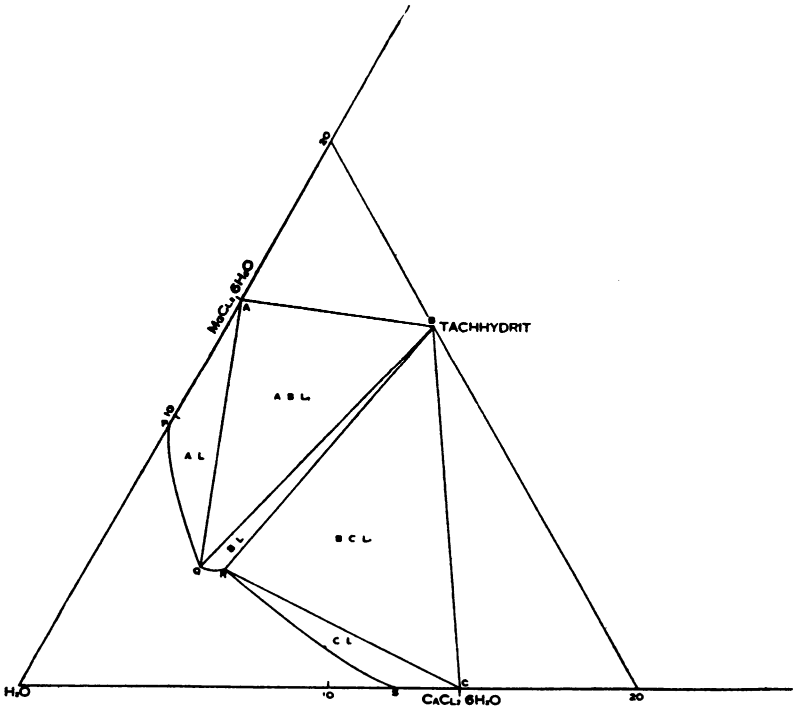

Fig. 2.—Portion of diagram for the ternary system $H_2O-MgCl_2-CaCl_2$, representing schematically the solubility isotherms at 23° under a pressure of 1 atm.

If, starting from the equilibrium *ACBL* at 21°.95, we raise the temperature by 0°.2, we must raise the pressure by 11.8 atm. in order to prevent the disappearance of any of the four phases; this relation was experimentally determined, so that the direction of this particular 4-phase line at 22° is known. Investigation of the combination *BCL* at higher temperatures (at 1 atm.) showed that at 25° a second 4-phase line is met; at this temperature, therefore, we have in equilibrium *BCDL*, where *D* stands for the solid phase ($CaCl_2 \cdot 4H_2O$). Thus the reaction ($CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$) + ($CaCl_2 \cdot 6H_2O$) = ($CaCl_2 \cdot 4H_2O$) + solution now takes place, and instead of III (*BCL*) we then have the combinations *DLC* or *DLB*. For instance, at 28°2 ($CaCl_2 \cdot 4H_2O$) and ($CaCl_2 \cdot 6H_2O$) are in equilibrium with solution of the composition $100H_2O$, 14.4 $CaCl_2$, 1.37$MgCl_2$. The relation between *P* and *T* for the 4-phase equilibrium *CDBL* is not known; but by analogy we may consider that its general course is similar to that of the curve for *ACBL*.

All of these relations are exhibited in the subjoined figure (Fig. 3), which represents a part of the ideal figure. From it we see again how relatively small temperature changes and large pressure changes alter the type of the 3-phase, and also of the 2-phase, combinations.

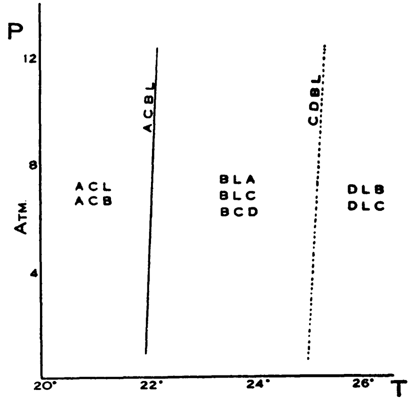

FIG. 3.—Portion of *PT* projection for system $H_2O \cdot MgCl_2 \cdot CaCl_2$, representing the stable 3-phase groupings and two 4-phase lines.

Consideration of an ideal case.—Let us suppose that between the four minerals *ABCD*, whose compositions may be expressed in terms of the three components *K*, *L*, and *M*, the relation $n_1A + n_2B \rightleftharpoons n_3C + n_4D$ exists;[1] it being assumed further that there are no false equilibria or unstable combinations. At arbitrary pressure and temperature only three of these can coexist; let the right-hand side be favored by lowering of temperature and of pressure. Then at low temperatures and small pressure, we should have the stable combinations *ABC* or *ABD;* at high temperatures and pressures, *CDA* or *CDB*.

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[1] This equation is analogous to the equation already given for the system $CaCl_2 \cdot MgCl_2 \cdot H_2O$. The complete analytical presentation of the relations for ternary systems is given by Schreinemakers in *Heterogene Gleichgewichte*, III, 210 f., which the reader desirous of fuller information with regard to ideal cases is advised to consult. (This book forms the third volume of the treatise, of which Vols. I and II only were completed by Roozeboom.)

Let us assume further that the minerals X, Y, Z are stable both above and below this inversion point, that they are made up of other components and do not affect the equilibrium relations of $ABCD$. We could then have the rocks $XYZABC$ (I), $XYZABD$ (II) on the one hand, $XYZCDA$ (III), $XYZCDB$ (IV) on the other. These four types are the ideal ones in the temperature, pressure and concentration region characterized by the relation $n_1A+n_2B \leftrightarrows n_3C+n_4D$. Now if a rock of type I comes into the temperature and pressure regions of types II or III, then D must be formed and either A or B must disappear.

Now the relations in actual metamorphic processes are complicated by a number of factors: that the rate of reaction is often small, that metastable forms occur, or that false or partial equilibrium only is attained. Hence we cannot know if a relation observed in the study of thin sections of a series of rocks is really characteristic of the temperature and pressure conditions which obtained during the process of metamorphism. Nevertheless, although the whole transformation may be metastable, it may be profitable to consider the ideal relation involved.

On the other hand, the formation of a variety of combinations is favored by the circumstance that pressure and temperature change during the metamorphic process and that the co-ordinates of the invariant point of neighboring and chemically very similar rocks may be different. Indeed in geologic units one seldom finds the production by metamorphism of a single type of mineral composition; instead of this there is usually a whole series, the individual members of which are closely interrelated. To take a few examples which have been investigated, there are: the hornblende porphyroblastic schists of Tremola[1] (Gotthard, Switzerland); the glaucophane schists of Syra[2] (Greece) and of the Val de Bagne[3] (Wallis, Switzerland); the chloritoid schists of the Garvera[4] region (Gotthard); the eclogites of the Ötztal[5] (Tyrol), etc.

[1] L. Hezner, *Neues Jahrbuch f. Min.*, Beilage Band XXVIII (1908), 157.

[2] H. S. Washington, *Am. Jour. Sci.* (4), XI (1901), 35.

[3] T. Woyno, *Neues Jahrbuch f. Min.*, Beilage Band XXXIII (1911), 130.

[4] P. Niggli, *Beiträge geol. Karte Schweiz*, N.F., XXXVI (1912).

[5] L. Hezner, *Tsch. Min. Petr. Mitteil*, XXII (1903), 437, 505.

In concluding this section we wish to state again our precise standpoint with reference to the application of the phase rule. To say that the phase rule must always hold for metamorphic systems is equivalent to the assumption that such systems always attained a state of equilibrium; which is certainly not true. Many rocks will be found to contain a larger number of minerals than the maximum number required by the phase rule. On the other hand, the fact that the number of minerals found agrees with this maximum is absolutely no criterion of the attainment of a state of stable equilibrium within the system; for at equilibrium there will in many cases be present fewer phases than this maximum number. One may say only that the rocks will show a tendency toward equilibrium, that they will tend to attain the state corresponding to the ideal *PT* diagram; the ideal types therefore are to be considered merely as representative examples which also will be of use in classifying actual rocks.

Consideration of ideal types may also be of great advantage in classifying metamorphic rocks; just as in the classification of crystals the ideal crystal form is used, although it is seldom that two crystals of the same substance separate out in precisely identical form. As an instance of its use in this way we may recall the well-known work of V. M. Goldschmidt on the contact rocks of the Christiania region.

The foregoing treatment applies only to cases where the metamorphic process has not been accompanied by any change in the gross composition of the material; the question of what happens in such case is taken up later. Here we will remark only that it is by no means necessary that rocks which *now* show identical chemical compositions should be made up of the same mineral constituents; for the reason that differences, and comparatively slight differences, in the amounts of volatile components ("mineralizers") *originally* present might easily alter the character, and order of separation, of the minerals formed in the metamorphic process.

THE GENERAL EFFECTS OF NON-UNIFORM COMPRESSION

The effects produced by exposure to non-uniform compression are in general permanent; that is, the original state of the system is not re-established when the compression ceases. The effect of differential compression may be resolved into two parts: that due to a (smaller) uniform pressure and that due to a shearing stress, the latter being the preponderating effect. The mere fact that "flow" or deformation of the compressed material occurred is sufficient evidence that unequal stresses were set up; in other terms, that the compression was not uniform. In discussing this question it will be convenient to treat first the effects of stress on a solid phase alone before passing on to the consideration of systems solid-liquid or of those in which we may imagine the appearance of a liquid phase to be one of the results of stressing the solid phase; the latter is much more fundamentally important in relation to metamorphic processes than the former.

The effects of stress on the solid phase alone.—The effects of stress on solids are what we are accustomed to call mechanical; they are subsidiary, rather than essential, in metamorphic processes. For this reason, and because the general subject has been discussed by Willard Gibbs, while its geological applications form the subject of a number of well-known papers,[1] the effects of stress on solids will be treated very briefly here.

Any directed stress acting on a particle may be resolved into three stresses, each acting on an element of surface in one of the three principal planes. These three stresses are represented both in direction and intensity by the three principal axes of an ellipsoid. The stress produces in the particle a strain, which will tend to change the shape of the particle, or its size, or both together. At any point there will be three mutually perpendicular directions in which the displacement is a maximum or minimum and about which these displacements will be symmetrically arranged as an ellipsoid is about its three axes. A homogeneous isotropic sphere exposed to the action of a stress will assume the form of the so-called strain-ellipsoid, the position of which, and thus the state of strain, at any point is completely determined.

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[1] C. R. Van Hise, "Metamorphism of Rock and Rock Flowage," *Bull. Geol. Soc. Am.*, IX (1898), 269; G. F. Becker, "Finite Homogeneous Strain Flow and Rupture of Rocks," *Bull. Geol. Soc. Am.*, IV (1893), 13; "Schistosity and Slaty Cleavage," *Jour. Geol.*, IV (1896), 429; "Experiments on Schistosity and Slaty Cleavage," *Bull. U.S. Geol. Survey 241* (1904); C. K. Leith, "Rock Cleavage," *Bull. U.S. Geol. Survey 239* (1903); L. M. Hoskin in *16th Annual Report, U.S.G.S.*, Part I, 1896; P. Niggli, *Beiträge geol. Karte der Schweiz*, N.F., XXXVI (1912).

The strain- and stress-ellipsoids are parallel to one another only in isotropic media, and then only when the stress acts continuously in a definite direction. The presence of particles of unequal hardness —in other words, heterogeneity of the material—results obviously in the cessation of this parallelism. The position of the strain-ellipsoid is influenced by the exact distribution of the particles of unequal hardness; and, on the other hand, the position of these fine layers—in so far as it can change at all—is determined by the direction of the strain-ellipsoid (tectonic displacements). The orientation of newly formed mineral grains is determined in general by the relations of stress and strain, the most thorough adaptation being attained when flow cleavage takes place. In the crystalline schists formed under stress which show heteroblastic structure the orientation of the porphyroblasts is indefinite, which is presumably due to their rate of formation. That their orientation does not correspond to the conditions of strain is evident from the fact that subsequent rotational movements have sometimes occurred,[1] accompanied by cataclastic phenomena. Cataclastic effects predominate in the so-called mylonitized rocks, which are found principally where thrusting has taken place.

The optical properties of crystals are influenced by stress. Isotropic minerals may become biaxial, if the direction of the principal stress does not correspond with that of the axes of symmetry. Uniaxial crystals become optically biaxial when the direction of the stress is other than that of the optic axis of the crystal; for instance, in crystalline schists quartz occurs frequently as optically biaxial crystals, which at the same time show elliptical, in place of circular, polarization, and undulatory instead of definite extinction. Application of stress changes in general the position of the principal axes of biaxial crystals; when the stress-ellipsoid is parallel to the ellipsoid derived from the crystalline axes there will be a change only in the refractive indices and in the optic axial angle.

Furthermore, stress may to some extent produce gliding or translational displacements in the individual mineral grains. As instances of the phenomena of gliding, calcite frequently is found twinned in the $(10\bar{1}2)$ plane; diallage also frequently exhibits lamellae which have resulted from stress. Translational displacements are those in which the displaced portion remains parallel to its original position; this phenomenon is shown—though usually only to a small extent—by plastic crystals, such as cyanite, augite, mica, graphite, calcite, brucite, when they occur in metamorphic rocks.[1]

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[1] P. Niggli, *Beiträge geol. Karte Schweiz*, XXXVI (1912), 61.

On the other hand, many crystals found in crystalline schists are the net result of a more or less thoroughgoing destruction of the original configuration of the system and of more or less shattering of the individual crystals, followed by a healing-up of the cracks and spaces thus produced. To account for this we are led to consider the effect of stress on the processes of fusion and solution.

Effects of stress on systems solid-liquid.—It has been shown in two previous papers[2] (to which the reader desirous of a fuller discussion of this topic is referred) that the observed effects of non-uniform compression can be satisfactorily correlated by ascribing them to the action of "unequal" pressure, that is, to a pressure which, in a system solid-liquid, acts on the solid phase but not, or not to the same extent, on the liquid phase. It can readily be shown from thermodynamic reasoning that the effect of unequal pressure is *always* to lower the melting point (or raise the vapor pressure, and hence the solubility) of a substance, and by an amount which is many times as great as the effect (raising or lowering) produced by the same pressure acting on both phases simultaneously.

The principle that unequal pressure lowers the melting-point was formulated first in 1881 by Poynting,[3] who applied it only to calculate the effect on the melting-point of ice. In 1892 the result was stated by Le Chatelier,[4] who applied it to several problems of geological interest—to the regelation of ice and the consolidation of beds of gypsum.

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[1] See papers by O. Mügge, e.g., *Neues Jahrbuch f. Min.*, I (1898), 71; II (1899), 55; also L. Milch, *ibid.*, I (1909), 60.

[2] J. Johnston, *Jour. Am. Chem. Soc.*, XXXIV (1912), 788; *Z. anorg. Chem.*, LXXVI (1912), 361; J. Johnston and L. H. Adams, *Am. Jour. Sci.*, XXXV (1913), 205; *Z. anorg. Chem.*, LXXX (1913), 281.

[3] *Phil. Mag.* (5), XII (1881), 32.

[4] *Z. physik Chem.*, IX (1892), 335.

In a paper[1] first published in 1894, E. Riecke discussed the effect of a one-sided pressure (a stress) on the melting-point of ice, and quite recently he has restated his conclusions in a second paper.[2] Riecke's formula for the lowering of melting-point of ice effected by the stress Z (tensile or compressive) is

$$\Delta T_1 = -\alpha Z^2$$

where (for ice) α has the value 0.00036 when Z is expressed in kg. per sq. cm.[3] He appears to consider this formula, which was developed for the case of a single crystal only, valid only for small values of Z; so that its range of applicability is somewhat limited. It has, under the name of the Riecke principle, been adduced occasionally by geologists[4] to aid in correlating observations connected with metamorphic processes and results.

The basic principle underlying Riecke's reasoning is identical with that used in the derivation of the equation used in the present paper, which, as mentioned above, was derived first by Poynting; but the latter, which is derived from general thermodynamic principles without specific assumptions (other than those common to all thermodynamic reasoning), is much more generally applicable, holding as it does for solid aggregates, and for any range of pressures, subject always of course to the condition that the pressure acts on the solid phase, but not, or to a less extent, on the liquid phase produced by melting or by solution.

Derivation of the formula: The derivation of the formula by means of which the effect of unequal pressure on a substance is computed is based on the thermodynamical fact that unequal pressure acting on any phase increases the "activity" of that phase, or its tendency to pass over into another phase; in other terms, unequal pressure acting only on the solid phase increases its vapor pressure and its solubility (in any particular solvent) and lowers its melting-point. Into the steps in the derivation of this formula it is unnecessary to enter here;[1] the final differential equation is:

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[1] *Nachr. Ges. Wiss. Göttingen*, 1894, 278; *Ann. Physik*, LIV (1895), 731.

[2] *Centralblatt Min. Geol.*, 1912, p. 97.

[3] 1 atmosphere = 1.033 kg. per sq. cm.

[4] For instance by Grubenmann, *Die kristallinen Schiefer*, 2 Aufl. (1910), and by Becke, *Denkschriften Wien Akad.*, 7 Mai, 1903.

$$\frac{dT}{dP}=\frac{TV_s}{\Delta H} \tag{V}$$

which expresses the lowering of melting-point by unequal pressure in terms of the absolute melting-point (T) and the molecular volume (V_s) of the solid at the temperature and pressure in question and ΔH, the molar heat of fusion under those conditions. The quantities V_s and T are always positive, but ΔH (as here used) is always negative; hence application of excess pressure on the solid phase *always* lowers the melting-point.

If we compare the melting-point depressions (dT_1 and dT_2 respectively) produced by the same excess pressure (dP) acting on (1) the solid phase alone, (2) both phases; that is, if we combine equations V and I, we obtain the result

$$\frac{dT_1}{dT_2}=\frac{V_s}{dV}=\frac{V_s}{V_s-V_l} \tag{VI}$$

or, expressed in words, the ratio of the lowering of melting-point of the solid phase, when this alone is subject to a given pressure, to the alteration (raising or lowering) observed with the same (given) pressure acting uniformly on both phases is equal to the ratio of the (specific) volume of the solid phase to the change of (specific) volume on freezing.

This equation shows how many times greater the melting-point lowering is when the pressure acts only on the solid phase. For example, the melting-point of ice is lowered by unequal pressure 12 times as much (or 0°09 per atm.) as by uniform pressure (0°0075 per atm.); in general $\Delta T_1/\Delta T_2$ is much greater than 12, because the fractional change of volume accompanying melting is usually much smaller than it is in the exceptional case of ice.

The (unequal) pressure (ϕ, expressed in atmospheres) required to cause a substance to melt at the temperature T_2 can be computed if we can integrate equation V. We cannot perform this integration rigidly for lack of the necessary data on the variation of

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[1] It is discussed in another paper: see *Jour. Am. Chem. Soc.*, XXXIV (1912), 788-802; *Z. anorg. Chem.*, LXXVI (1912), 361-79.

ΔH and V_s with pressure and temperature; but fortunately the variation of $V_s/\Delta H$ is small and for the present purpose unimportant. We may therefore consider $V_s/\Delta H$ to be independent of pressure and temperature; by integration and transformation we then obtain the equation

$$\phi=95.1\, QD \log \frac{T_1}{T_2} \qquad \text{(VII)}$$

which gives the unequal melting-pressure (ϕ) at the temperature T_2 in terms of the heat of melting (Q, in calories per gram), the density D, and the ordinary melting-point at 1 atm. pressure (T_1, in absolute measure). At the present time the data requisite for the calculation of ϕ are available only for a few metals; these calculations have been made and the results are presented in Table III; the sixth column (headed ΔT_1) gives the melting-point depression[1] produced by 1 atm. excess pressure acting on the solid, the last (headed ϕ_{27}) contains the computed pressure (in atmospheres) which, acting on the solid alone, would be required to cause the substance to melt at 27°.

TABLE III

LOWERING OF MELTING-POINT OF METALS EFFECTED BY ONE ATM. UNEQUAL PRESSURE; TOGETHER WITH THE COMPUTED MELTING-PRESSURES (IN ATM.) AT ORDINARY TEMPERATURES

METAL	MELTING-POINT		HEAT OF FUSION Q	DENSITY D	ΔT_1	ϕ_{27}
	t	T_1				
K	62	335	15.7	0.87	0.59	64
Na	97	370	31.7	0.98	.29	266
Pb	327	600	5.4	11.37	.24	1,760
Sn	232	505	14.1	7.29	.12	2,200
Bi	270	543	12.5	9.80	.11	3,000
Cd	321	594	13.7	8.64	.12	3,300
Al	658	931	42.0	2.60	.21	5,100
Zn	419	692	28.0	7.1	.084	6,900
Ag	960	1,233	23.0	10.50	.12	14,000
Cu	1,083	1,356	43.0	8.93	.086	24,000
Pd	1,550	1,823	36.3	11.4	.11	31,000
Pt	1,755	2,028	27.2	21.5	0.084	46,000

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[1] As calculated by the formula $\Delta T_1=\frac{T_1}{41.30\,QD}$, which is easily derived from equation V.

By comparison of the above results with those of Table I we see how much greater the effect of unequal pressure may be. For example, take the case of lead, the melting-point of which is changed +0°.008 by 1 atm. uniform pressure, but −0°.24, or 30 times as much, by 1 atm. excess pressure on the solid phase.

The sequence of the metals when arranged in the order of their ϕ values (as computed from equation VII) is identical with that obtained when they are arranged in the order of their flow pressures or of any of their elastic properties (e.g., tensile strength, hardness). This parallelism is a striking corroboration of the effectiveness of unequal pressure in correlating phenomena attending the deformation of crystalline solids.[1]

It is of interest to inquire if there is any relation between the hardness of minerals and any of their other properties. There is a parallelism between the hardness of the metals (as ordinarily measured) and the calculated ϕ values, which depend upon the density, heat of melting, and temperature of melting. Of these three factors the first lies within comparatively narrow limits for a series of minerals; the second is not known, but probably lies also between comparatively narrow limits *in general*;[2] the limits within which the melting-point lies are comparatively much wider apart. Consequently, we should expect that there is a rough parallelism between the hardness of minerals and their melting-point.

That this expectation is justified is shown by Fig. 4, in which the melting-point of those minerals which give congruent melting-points is plotted against the hardness; this has been done for all minerals for which the necessary data could be found in Landolt-Börnstein *Tabellen*. All of the points lie within a zone the breadth of which is no greater than one might expect from the very uncertain nature of the measurements of hardness, and in view of the circumstance that the latent heat has not been taken into account. When the latent heat is taken into account (which is possible only for a few of the metals) and the ϕ values plotted against hardness the points lie within a very much narrower zone. From this we can infer that the same will be found for the minerals when the requisite data are known.

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[1] For a discussion of this question see Johnston, *Jour. Am. Chem. Soc.*, XXXIV (1912), 788; *Z. anorg. Chem.*, LXXVI (1912), 361.

[2] The exceptional cases would be those in which the heat of melting is very small.

There is therefore a considerable body of evidence then which suggests that any permanent deformation of a crystalline dry aggregate is determined by an actual melting of some part of the material—a melting which occurs as soon as the local stress reaches the melting-pressure corresponding to the temperature of the material—with subsequent resolidification; this resolidification consists in the production of crystals of that form which appears most readily under the particular conditions of pressure (and therefore not necessarily of the original form) and, so far as the argument is concerned, recrystallization need not be complete. So far as we are aware, there is no evidence which directly contradicts the above hypothesis; on the contrary this hypothesis enables us to correlate and interpret a large number of diverse and apparently contradictory observations.[1]

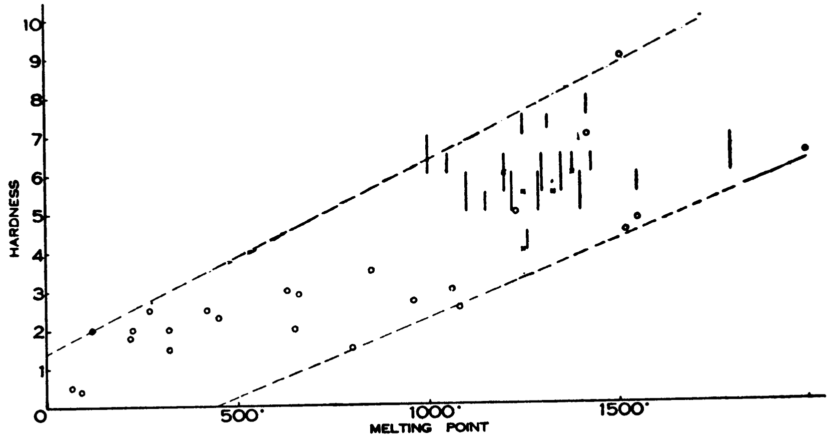

Fig. 4.—Diagram to exhibit the relation between hardness (as ordinarily measured) and melting-point. Circles represent elements; crosses or lines represent minerals, lines being used where the tables give a value such as 5.5—6.5.

This type of compression accounts easily for regelation; the most common example is the regelation of the substance water which, as it happens, is exceptional in that its freezing-point is lowered by uniform pressure. This phenomenon cannot in general be produced by uniform pressure because uniform pressure raises the melting-point of most substances; so that we shall with advantage consider unequal pressure to be the effective factor in the case of water as in that of other substances. Consider a block of ice at 0° supporting a loaded wire. The pressure exerted by the wire depresses the melting-point of the ice by an amount Δt; immediately beneath the wire, therefore, we have at any instant a thin layer of ice at $-\Delta t$ in equilibrium with water at $-\Delta t$. The water, however, escapes round the wire, and so comes into contact with ice at 0°; such a system is, however, unstable, for under these conditions water cannot remain subcooled. Consequently, the water freezes again and forms a solid block above the wire.

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[1] See Johnston and Adams, *Am. Jour. Sci.*, XXXV (1913), 205.

The process by which a mass of loose snow is compacted into a block of ice is identical with this. The pressure, due to the superincumbent material, lowers the melting-point at the surface of contact of adjacent grains; the water at $-\Delta t$ flows into the interstices where the pressure is smaller and freezes again. This process continues until the interstices are all filled up, that is, until a solid block of ice is formed. This again, we believe, is the general mode in which consolidation of a mass of originally loose material takes place, as for instance in the welding of metals and in pyrometamorphic processes. The consolidation of loose mineral material, however, takes place more usually through a process of solution, the general principle being identical in both cases; this we shall now consider.

Influence of unequal pressure upon the solubility of solid substances.—Considerations in every respect analogous to the foregoing are applicable to systems of a solid in contact with water or other solvent; in such cases, pressure acting in excess on the solid increases its solubility,[1] and thus renders the solutions supersaturated with respect to the *unstressed* solid. Le Chatelier[2] accounts in this way for the consolidation of natural beds of rock-salt, gypsum, calcium carbonate, and clay. To test this matter directly he compressed sodium chloride or sodium nitrate in contact with its saturated solution to about 200 atmospheres for a period of eight days, and found that blocks resembling rock-salt and marble were formed in this way. Similarly one can account for the formation of rigid sandstones from beds of originally loose sand.

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[1] The amount of this increase of solubility can be computed from equations analogous to those applicable to melting-points.

[2] *Z. physik. Chem.*, IX (1892), 335.

Application to metamorphic processes.—The processes just discussed have a very important bearing on rock metamorphism wherever stress has been an important factor. The unequal pressure increases the activity of the solid components, and fusion or solution occurs wherever the local stress reaches the appropriate value. In this way larger amounts of material come into local solution to be immediately redeposited (at points where the stress is smaller) in the form characteristic of those particular conditions, and hence not necessarily in the original form; consequently reactions occur more readily in stressed rocks. The nature and form of the new crystals depend therefore upon the relations of stress and strain in the mass. The so-called Riecke principle has been adduced in this connection; but the whole question has been handled in a much more general way by Willard Gibbs,[1] from whom we quote the following sentences:

> If a solid which is homogeneous in nature and in state of strain is bounded by six surfaces perpendicular to the principal axes of stress, the mechanical conditions of equilibrium for these surfaces may be satisfied by the contact of fluids having the proper pressures, which will in general be different for the different pairs of opposite sides, and may be denoted by p', p'', p'''. It will then be necessary for equilibrium with respect to the tendency of the solid to dissolve that the potential for the substance of the solid in the fluids shall have certain values μ', μ'', μ''', which are entirely determined by the nature and state of the solid.

From Gibbs' equations it follows directly that μ' is "greater than the value of the potential which would be necessary if the solid were subjected to the uniform pressure p'" (and similarly with μ'', p'', μ''', p''').

> That is, the fluids in equilibrium with the solid are all supersaturated with respect to the substance of the solid, except when the solid is in a state of hydrostatic stress [uniform pressure]; so that if there were present in any one of

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[1] "Equilibrium of Heterogeneous Substances," *Collected Papers*, pp. 196–97. The question was first treated by James Thomson, *Trans. Roy. Soc. Edinburgh*, XVI, 575; *Proc. Roy. Soc.*, XI, 473; *Phil. Mag.* (4), XXIV, 395.

> these fluids any small fragment of the same kind subject to the hydrostatic pressure of the fluid, such a fragment would tend to increase. Even when no such fragment is present. . . . . the presence of the solid which is subject to the distorting stresses will doubtless facilitate the commencement of a solid of hydrostatic stress upon its surface. . . . . But in the case of a solid of continuous crystalline structure, subjected to distorting stresses and in contact with solutions satisfying the conditions deduced above . . . . within certain limits the relations given must admit of realization, especially when the solutions are such as can be easily supersaturated.[1]

In other words, when a crystal is strained, the solubility on the strained face is increased. Consequently material tends to dissolve off the strained faces of a crystal in contact with a saturated solution in any solvent, and to be redeposited where the strain is less.[2] The effect of this is that the crystal changes in such a way as to diminish the stress upon it—an example of the well-known principle that the readjustment of a system following disturbance of equilibrium is always such as to minimize the effect of the disturbing factor.

In order to illustrate how stress affects crystallization let us suppose an isotropic sphere exposed to stress. The stress may be resolved into three stresses acting along axes mutually perpendicular; the sphere is thereby deformed into an ellipsoid, the axes of which in the simplest case coincide with those of the stress-ellipsoid. The final effect is the same when the substance is immersed in a solvent medium, for the solubility is increased most in a plane perpendicular to the greatest stress.

Let us consider now the growth under stress of new isotropic particles. The stress would tend to make the particle ellipsoidal, even though it were to make equal growth in all directions. But the saturation limit is reached soonest in the plane perpendicular to the smallest stress, so that the isotropic particle in growing assumes of itself the form of the strain-ellipsoid. From this it follows that particles growing in a stressed medium will be flattened in a direction perpendicular to the greatest stress and will be paral-

[1] W. Gibbs, *loc. cit.*

[2] This does not necessarily imply that the material be redeposited on the unstrained faces of the original crystals; it may go to form new individuals. In very many cases, of course, a reaction or transformation will occur, so that the material will not be redeposited in its original form.

lel to one another; their arrangement thus corresponds exactly to flow cleavage.

The anisotropic character of minerals (also with respect to their solubility relations) introduces a complication, without, however, affecting the general principle involved. A definite arrangement of minerals with respect to a single vectorial property is often found; such an arrangement can of course only be ascribed to the vectorial properties themselves, whether they be differences in solubility or in cohesion.

In metamorphic rocks exhibiting flow cleavage the flakes of mica lie in such a way that the smallest growth was perpendicular to the base, the greatest growth in the basal (and cleavage) plane. We must remember that the immediate influence of stress and strain is made evident in an unequal development in different directions, although the general principle alone gives us no information as to the particular vectorial direction which is parallel to the smallest development. But when we take into account the anisotropy exhibited by the original tiny particles, we must include as one of the factors the orientation of the original particles with respect to certain directions within the crystal; those directions, namely, parallel to the plane (gliding plane) in which displacement of the crystal particles is most readily effected, and perpendicular to the plane (cleavage plane) in which the crystal most readily splits. When the rates of growth or the solubility relations are anisotropic, specific effects analogous to the above will be produced; but of this influence little that is definite can at present be said except that it certainly is appreciable.

From this it follows that the relicts will tend to assume the form of the strain-ellipsoid (if we neglect for the moment the complications introduced by anisotropy). And indeed it is well known that the quartz relicts in rocks originally conglomerate are more or less oval in form. Further, the recrystallization will tend to take place in such a way that the strain is a minimum. This is the basic principle underlying the phenomenon of flow cleavage; for it corresponds to minimum expenditure of work in producing the new formation, or in other words it represents the most complete adaptation of the system to the strains acting upon it.[1] The flow of rocks has been studied experimentally, notably by F. D. Adams and his collaborators;[1] it resulted always in the production of a kind of cleavage.

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[1] P. Niggli, *Beiträge geol. Karte Schweiz*, N.F., XXXVI (1912), 46.

It is characteristic of those cases of metamorphism where stress has been the predominant factor that the system, taken as a whole, is not in simple equilibrium, but rather in a stationary condition only. Now since, as we have seen, unequal stress acts mainly by depressing the melting-point and by raising the solubility, it follows that its effect on the transformation solid-solid is very small. Consequently we might expect that the forms produced under unequal stress would often be forms which cannot be obtained from ordinary melts; and this indeed is often observed.

Let us compare the mineral composition of the crystalline schists (which have very often been formed under stress) with that of eruptive rocks or with metamorphic rocks of the Katazone, making use of the summary given by Grubenmann[2] (see p. 613).

From this summary it is evident that many of the minerals occurring in rocks which have been subjected to unequal stress occur also as ordinary products of the secular alteration of magmatic minerals at low temperatures. The water content of many of them determines in large part their behavior when heated or melted under ordinary conditions. Nevertheless the paragenesis of the stress minerals is, as Grubenmann has pointed out, characteristic of relatively low temperatures. Stress has increased the "activity," so that in stressed systems some reactions readily take place which otherwise would go very slowly. Thus unequal stress may be regarded as a kind of catalytic agent, though in thinking of it in this way one must remember that it has frequently a characteristic influence on the nature of the products of a reaction, in addition to its influence on the rate of formation of those products.

In spite of the fact that in stressed systems we are not dealing with simple equilibrium conditions, we may apply principles similar to those set forth on p. 597 to ideal typical systems. In doing this we would consider only a simple equilibrium characteristic of relatively low temperatures, remembering always that the conclusions reached by this means are subject to considerable limitation; still such conclusions may be useful for purposes of classification, if for no others.

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[1] *Phil. Trans. Roy. Soc. London*, A, CXCV, 363; *Am. Jour. Sci.*, XXIX (1910), 465; *Jour. Geol.*, XVIII (1910), 489; *XI Congrès geol. internationale*, II (1910), 911.

[2] *Die kristallinen Schiefer*, 2. Aufl., 1910.

Main Components	Stress Mineral	Corresponding Minerals in Katamorphic Rocks or in Eruptive Rocks	Products Obtained on Heating or Fusing the Stress Mineral
$H_2O, Al_2O_3, K_2O, SiO_2$......	Sericite	Alkali feldspar, muscovite?	Leucite, nephelitic mineral, glass
$H_2O, Al_2O_3, K_2O, MgO, FeO, SiO_2$..................	Biotite	Biotite	Olivine, spinel, leucite(?), glass
H_2O, MgO, FeO, SiO_2.....	Chlorite	Partly biotite, partly olivine, spinel, augite	Spinel, olivine +?
$H_2O, FeO, SiO_2, Al_2O_3$......	Chloritoid	Cordierite+sillimanite, spinel	....
$H_2O, FeO, Al_2O_3, SiO_2$.....	Staurolite	Same as chloritoid	....
$H_2O, Fe_2O_3, Al_2O_3, CaO, SiO_2$	Epidote	Consist of plagioclases in combination with pyroxenes, etc. Epidote is also a primary constituent of some granites	Anorthite and lime-augite
$H_2O, Al_2O_3, CaO, SiO_2$.....	Zoisite	Consist of plagioclase	....
H_2O, CaO, MgO, SiO_2......	Nephrite, actinolite	Augite and olivine	....
$H_2O, MgO, FeO, CaO, Al_2O_3$ alkalies, SiO_2...........	Hornblendes	(In part) basaltic hornblendes or pyroxenes	Pyroxene+olivine
$Na_2O, Al_2O_3, SiO_2\left\{\begin{matrix}FeO\\MgO\end{matrix}\right\}$...	Glaucophane	?	?
$CaO, MgO, FeO, Al_2O_3, SiO_2$	Garnet	Garnet, plagioclase, olivine, pyroxene	Anorthite, monticellite, melilite, olivine, meionite
Al_2O_3, SiO_2..............	Kyanite (Andalusite)	Sillimanite, andalusite	....

Influence of stress on reactions accompanied by the production of a vapor phase.—In considering the effects of stress it is absolutely essential to note that the influence of stress on reactions which are accompanied by the evolution of a gas or vapor is enormous. For instance, it is well established that continued grinding in a mortar of minerals containing water or even of substances containing water of crystallization results in a loss of water;[1] thus apophyllite on grinding lost about 1 per cent of water (Thugutt), $MgSO_4 7H_2O$ lost about 2.5 per cent H_2O (Blecker). Moreover, Johnston has found[2] that some carbon dioxide can be driven off from a substance as stable as calcium carbonate by grinding it in a mortar for a few minutes; in this case the grinding lowers the temperature at which the calcium carbonate exhibits an appreciable pressure of carbon dioxide by some 500°.

This behavior is in thorough accordance with the standpoint adopted with regard to the effects of unequal pressure. Application of precisely similar reasoning leads to a formula entirely analogous to equation V, namely:

$$\frac{dT_p}{dP}=\frac{T_p V}{\Delta H} \qquad (\mathrm{V}a)$$

where T_p is the temperature corresponding to a given pressure of the vapor phase, ΔH the heat of reaction, and V a (specific) volume, which practically will be intermediate between that of the original solid and the volume change accompanying the reaction. Furthermore, we see that the unequal pressure required to produce an appreciable pressure (p) of the vapor phase at a given temperature would be approximately proportional to $Q \log T_p$,[3] T_p being the temperature at which the system in the unstressed condition would exhibit the vapor pressure p, and Q the heat of dissociation; and this conclusion is roughly borne out by the observations hitherto recorded.

Analogous considerations apply to reactions such as $RCO_3 + SiO_2 \rightarrow RSiO_3 + CO_2$; the general conclusion being that unequal stress will cause reactions between solids accompanied by the development of a gas phase to proceed to an extent which would be inappreciable in the absence of stress. This renders it evident, as has been noted on a previous page, that great care must be exercised in choosing points for purposes of a geologic thermometer; for the only points really adapted to this purpose are transitions solid-solid (which, moreover, must not be much affected by uniform pressure), while systems in which a vapor phase intervenes are altogether useless for this purpose.

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[1] Mauzelius, *Sveriges Geol. Undersökning Arsbok*, I (1907), No. 3; W. F. Hillebrand, "Influence of Fine Grinding on the Water and Ferrous Iron Content of Minerals and Rocks," *Jour. Am. Chem. Soc.*, XXX (1908), 1120; *Chem. News*, XCVIII (1908), 205, 215, who refers to some earlier observations; S. J. Thugutt, *Centr. Min. Geol.* (1909), p. 677; I. B. Blecker, *Chem. News*, CI (1910), 30.

[2] A separate note dealing with this question is in course of preparation.

[3] Since from one substance to another there is comparatively little variation of V, but large variations of Q and T_p.

METAMORPHISM ACCOMPANIED BY ADDITION OF MATERIAL

Hitherto we have considered only those cases of metamorphism where there was no addition of material during the process; this limitation permits us to consider the changes produced in a given chemical system by a change in its physical conditions and environment. As a matter of fact, chemical investigation of metamorphic rocks[1] has shown that in many cases the gross composition of the original eruptive or sedimentary rocks has remained sensibly unaltered by the metamorphic processes;[2] in other cases, on the other hand, it has shown that an addition of material did occur during the process of metamorphism.

Now the addition of material, whether temporary or more or less continuous during the process, is often the main cause of the changed physical conditions, therefore the cause of the metamorphic process. When this is so the chances for a complete transformation of the rock are in general more favorable than when temperature and pressure alone are variables. Thus it is that in rocks which have been metamorphosed with, or by, the addition of foreign material there are peculiarities in mineral content and often in texture and structure. In all such cases it is to be noted that the gross composition of the rock *now* can give us no certain idea of the composition of the system during metamorphism, and therefore that two rocks which now have the same bulk composition may then have represented quite different chemical types.

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[1] Grubenmann, *Die kristallinen Schiefer*, II. Teil, 2. Aufl., 1910.

[2] The occurrence of small changes of composition, such as have been noted, e.g., by J. D. Trueman (*Jour. Geol.*, XX, 228 f.), is an occasional, but certainly not a general, phenomenon. Such small changes exert no marked specific influence on the general result, and consequently are not specially discussed here.

The term metamorphism with addition of material we reserve for the changes characterized by a penetration of the original rock by some foreign system; we do not use it to denote the small local changes in concentration which may have taken place. The foreign system, the viscosity of which must be comparatively small, will generally be of magmatic origin; we must therefore briefly consider magmatic processes.

Magmas are mixed solutions of silicates, charged with volatile substances, the so-called gas mineralizers, the amount of which, varying with the progress of the intrusion and solidification, depends upon the previous history and original composition of the particular magma basin. Of these volatile components, the majority can exist, *when alone*, only as gases at the temperature at which the magma crystallizes.

Analysis of volcanic exhalations has led to the recognition of the following gases and vapors, excluding those of minor importance: H_2O, H_2, N_2, CO_2, CO, H_2S, SO_2, HCl, Cl_2, CH_4, HF, SiF_4. Which of these appear under given conditions depends mainly upon temperature and pressure, the latter especially, since it influences the equilibrium greatly when the reaction is accompanied by a change in the total number of molecules (especially therefore in cases of dissociation or association). Conversely, reaction will frequently take place in gaseous systems when the pressure changes, therefore in magmatic gases when they escape into a region of lower pressure. Such reactions are often attended by a large evolution of heat, which is doubtless one of the sources of heat, and possibly even one of the causes of volcanic outbreaks. For any reaction which evolves much heat and proceeds very rapidly may be explosive; for instance, hydrogen and oxygen explode when set off by a spark, that is, when the reaction is started at a high temperature (where its rate is very great), the amount of heat evolved by the reaction being sufficient to prevent a lowering of the temperature of the zone reacting at any moment. When one takes into account the reactivity of gases and the dependence of the position of equilibrium at any moment upon the effective temperature and pressure at that time, one is led irresistibly to the view that from the gases found in the exhalations no safe conclusion can be drawn as to the nature of the gaseous phase present in the intrusive magma unless the conditions existing there and their influence upon the equilibrium are all known. Nay more, it is to be expected that the exhaled gases do not represent an equilibrium at all, but are actively in the process of reacting.[1]

The magma also contains, in addition to the above gases and vapors, a number of other substances which are volatile at high temperatures, such for example as metallic sulphides, chlorides or fluorides, and compounds containing boron.

It is not at all necessary that the gaseous components, such as H_2O, H_2S, HCl, SO_2, exist as gases in the magma, even when they are present in the free state and not as compounds. For in that case it is their miscibility with the magma—or in other words, their solubility in it under the particular conditions (of which pressure is obviously the most important)—which determines whether they are present in the liquid phase.

The critical temperature, above which a system can exist only as gas, is a function of the chemical composition of the system. A gas when dissolved in a mixture of non-volatile components will exhibit a higher critical temperature than it does in the pure state; such a solution would of course exert in general a considerable gas pressure, which, however, need not be as great as the critical pressure of the volatile component in the pure state.[2] To illustrate: the critical temperature of SO_2 is 157°.5, its critical pressure is 79 atm. Now if 24.7 parts $HgBr_2$ (the melting-point of which is 236°.5) and 75.3 parts SO_2 are heated in a sealed glass tube, the volume of which is so chosen that the pressure will be about 80 atm. at 157°, melting of the $HgBr_2$ takes place at 230°.[3] This lowering of 6°.5, which is due to the taking-up of SO_2 by the melt, shows that at a pressure of about 100 atm. a considerable quantity of SO_2 is condensed or dissolved in a melt of $HgBr_2$ at 230°, in spite of the fact that the critical temperature of pure SO_2 is 157°5.

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[1] Day and Shepherd, for example (in the course of an investigation as yet unpublished), find that the gases emerging from the volcano Kilauea contain CO, CO_2, S, SO_2, H_2O, H, Cl, and F—a mixture of gases which cannot possibly coexist in equilibrium.

[2] A full discussion of these matters will be found in P. Niggli, *Z. anorg. Chem.*, LXXV, 161; LXXVII (1912), 321; *Central. Min.*, 1912, p. 321; *Geol. Rundschau*, III (1912), 472. The main points, especially in case the volatile component is water, are treated by Morey and Niggli, *Jour. Am. Chem. Soc.*, XXXV (1913), 1086 f.

[3] *Z. anorg. Chem.*, LXXII (1912), 161 f.

In precisely the same way we can have at high pressures water, or any of the other gases, present in the magmatic melt, and at the same time lowering its melting-point considerably below what it would be were no volatile components present.[1] Initially the amount of volatile component might be small, but its proportion in the liquid would increase (if the pressure remained constant, i.e., unless gas can escape) as crystallization progressed, unless the gas itself entered largely into the solid minerals.

On the other hand, gaseous material at high pressures and at temperatures above the critical can exert some degree of solvent action, as is evident from the following reasoning. The volatile component A as liquid can dissolve the non-volatile component B. Now unless the solubility of B in liquid A diminishes very rapidly near the critical point, there will be at that point a definite amount of B in solution. But since at the critical point the liquid and gaseous phases are by definition identical, there must then be the same proportion of B in the gaseous phase; so that above the critical temperature we can have a gaseous, or better a fluid, solution of a non-volatile substance. In general there is a very marked falling-off in solubility just below the critical point, but this in itself is no reason why at still higher temperatures and pressures the solubility of B in A should not again increase.

For instance, in fluid SO_2 at 159°4 and at a pressure of about 80 atm. the solubilities of $HgBr_2$ and HgI_2 are respectively about 1.5 per cent and 0.7 per cent by weight. At 230° in the same volume (hence at correspondingly higher pressures) the amount of $HgBr_2$ dissolved is about 8.5 per cent, while at 254° about 6.2 per cent HgI_2 dissolves in the fluid phase. This example illustrates only the possibility of the phenomenon; the quantitative results cannot of course be transferred to magmatic systems. But the two cases are entirely analogous in principle, and the residual phase from solidification of the magma, even though it be gaseous, is to be looked upon as a solution.

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[1] Direct evidence bearing on this point will be presented in the near future.

Under magmatic conditions the volatile substances (such as H_2O, SO_2, CO_2, etc., all of which are to be treated in exactly the same way) may in part unite with some of the other constituents to form more or less stable compounds which may be liquid under the conditions of temperature and pressure obtaining. The proportion combined in this way is controlled by temperature and pressure, the effect of the latter being to raise the concentration in the gas phase and hence, in accordance with Henry's law, in the liquid phase also. An idea of the influence of temperature is afforded by the following recently obtained results: in a melt of 1 mol. K_2O and 0.94 mol. SiO_2 heated in an atmosphere of CO_2 at 1 atm. pressure there is at equilibrium at 900,° 0.33 mol. CO_2 present as carbonate, while at 960° and 1000° the corresponding amounts are 0.28 and 0.24 mol.[1]

In the magma, therefore, the proportion of gas and liquid is a function of chemical composition, of temperature, and especially (because of its relation to concentration) of pressure. In the process of crystallization the concentration of that portion of the volatile components which does not crystallize out as compound or as solid solution will increase relatively in the residue. Eventually, therefore, a fluid solution under high pressure will remain, which will escape whenever an opportunity presents itself, as for instance along tectonic lines. When the volatile components can escape slowly but continuously they will obviously not be under very high pressure, and the amount of material carried by them will be small. Consequently in such cases the main effects are due to the change of temperature and the production of a more or less homogeneous medium by impregnation with the volatile components (especially when water is a factor), which results finally in a fairly uniform recrystallization of the original rock.

The extent of metamorphism is governed in large degree by the nature of the original rock; for instance, by its permeability, which is doubtless one of the chief reasons why limestones in contact with eruptive rocks are much more extensively metamorphosed, and contain a greater percentage of pneumatolytic minerals, than the shales. Moreover, its chemical composition may be a factor, if it is such that reaction may take place between any of its components and the penetrating gases (fluorides, sulphides, etc.). Furthermore, the conditions of formation of the original rock are of importance, as indeed they are with any metamorphic process; for if these conditions were not very different from those which obtained at the period of metamorphic action, the amount of this action would be slight, because there would be either no tendency toward another equilibrium or only an instability of single phases.

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[1] P. Niggli, *Z. anorg. Chemie* (in course of publication).

Usually in cases of contact metamorphism there is a small pneumatolytic addition of material, which may be temporary or permanent. If it consists essentially in a saturation with water vapor it will materially favor recrystallization. In the rock close to an eruptive contact there is often observed an increased concentration of alkalies, especially of soda. In sediments—clays and shales—there is usually more potash than soda, a predominance which is correlated with the relative solubility or stability of potash- and soda-minerals, since clastic sediments are in large measure merely residues, the least soluble portions of the original material under the particular conditions to which it has been subject. Contact-metamorphosed shales and schists, on the other hand, often have a much larger soda-content than the unaltered material of the same horizon, as is illustrated by the following analyses of rocks in the Christiania region, as given by V. M. Goldschmidt.

	Contact Metamorphic	Unchanged Schists from the Same Locality	
		1	2
SiO_2	54.95	54.43	49.46
TiO_2	1.15	.....	0.89
Al_2O_3	16.32	15.93	19.44
Fe_2O_3	2.95	8.42	1.37
FeO	5.66		6.03
MnO	0.16	.....	0.11
MgO	4.89	3.50	4.68
CaO	3.88	3.56	3.16
Na_2O	*5.56*	*0.74*	*1.55*
K_2O	3.56	3.44	4.12
C	.....	0.66	.....
Loss on ignition	0.71	7.19	6.37
FeS_2	.....	.....	0.29
CO_2	.....	.....	3.70
	99.79	97.87	101.17

The same observation has also been made by others, among them L. Hezner[1] in schists of the Gotthard region. In this case the additions did not take place at the period of intrusion, but during the tectonic disturbances, a fact which shows that the phenomenon is not due to a difference of volatility of soda and potash compounds at high temperatures, but to differences of solubility. Corresponding to this, the solutions emanating from eruptive rocks usually contain more soda than potash, a fact which is correlated with the high soda content of sea-water.

The occurrence of relatively small amounts of such substances as hydrofluoric acid, boric acid, hydrofluosilicic acid, which often are present in magmatic solutions and emanations, can be noted in the mineral content, though the general characteristics of the rock are otherwise altered but little. Such additions produce certain minerals characteristic of contact-metamorphic rocks: such as fluorite (F), scapolites (chlorides), axinite, tourmaline (B), ores (S, As, Sb), lime silicates or quartz in metamorphosed carbonates (Si).

If intrusion proceeds relatively rapidly, or if solutions (fluid or liquid) at high pressure remain over from the process of solidification, there will be an intensive penetration of the surrounding rock with magmatic material. The escape of the magmatic solution follows along the lines of least resistance, producing numerous veins and dykes; in originally sedimentary rocks the direction of these is that of the stratification, or in case the rock has been (or is simultaneously) subject to tectonic disturbance, they lie in the direction of the cleavage planes produced thereby. An interfoliation of the rock may therefore be produced in this way.

A further consequence of intense penetration with hot magmatic material is a considerable rise of temperature in the surrounding rock, which produces the characteristic phenomena of thermometamorphism and *Sammelkristallisation* (increase in size of the crystals). In the neighborhood of injected veins the crystals of a mineral are commonly larger than they are at some distance from it. The tendency to growth of crystals exists because small crystals of any substance are unstable with respect to larger crystals.

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[1] *Neues Jahrbuch f. Min.*, Beilage Band XXVIII (1908).

Growth actually takes place only when the temperature is high enough for the rate of growth to be appreciable.

The occurrence of this phenomenon in precipitates in contact with water is frequently used to advantage in analytical operations, to coarsen the grain of precipitates and so render them easier to filter. It has also been demonstrated on a system containing no water by Rinne and Boeke,[1] who, by heating up calcite crystals of various sizes in gas-tight bombs to high temperatures (1,000°) for considerable periods, found that the grains had become nearly uniform in size. Of similar import is the well-known fact that a glass may be made to crystallize in a temperature region in which it is by no means fluid, the optimum effect occurring usually at a temperature 20°–50° below its eutectic temperature.

When rock fragments are surrounded by liquid magma, it will act as a solvent and corrode the fragments in a manner depending upon the temperature and chemical composition of both. On the other hand, the solid particles act as crystal nuclei toward the magmatic solution, at least if its temperature is such that crystallization is possible. It is to be noted that rock transformations, due to partial meltings and recrystallizations, may take place at temperatures far below the melting-points of the individual minerals present; for such processes the positions of the various possible eutectic points are the essential criteria. Thus it is well known that mixtures of solid components in eutectic proportions can be liquefied by long-continued heating at the eutectic temperature, which may be very much lower than the melting-point of any one of the components.

The question as to whether solid fragments sink or float in the magma cannot be decided by density measurements made at ordinary temperature, but its answer involves a knowledge of change of volume with temperature, and requires, in addition, that the influence of viscosity and of gas evolution be considered.

R. Brauns has lately directed attention to a new type of metamorphism, the so-called pyrometamorphism, a term which he has used to denote the effects of hot gases in partially melting[2] some of the ejected blocks found in the Laachersee region. Such corrosion phenomena are also common, for instance, in biotites of injected rocks. This action of hot gases is identical with that of a blast flame, except that some addition of material may at the same time take place.

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[1] *Tschermak's Petr. Mitt.*, XXVII (1908), 293.

[2] This idea has also been made use of by Daly in his paper on "The Nature of Volcanic Action," *Proc. Am. Acad.*, XLVII (1911), 92–93.

CONCLUSION

In the foregoing pages we have endeavored to set forth the most important general principles concerned in rock metamorphism—a general term which includes a number of special cases (e.g., contact metamorphism) all of which, however, differ only in the degree of predominance of one (or more) of a definitely limited group of effective factors. These factors are: temperature, uniform pressure, stress (non-uniform pressure), and gross composition of the system at the time of metamorphism; the same, namely, which determine the equilibrium of the relatively simple chemical systems hitherto investigated experimentally. The knowledge gained from a study of these simple systems may be used as a basis for a prediction of the general character and significance of metamorphic processes; though in applying the principles one must always bear in mind those circumstances which oppose the attainment of a state of true equilibrium, such, for example, as slowness of reaction or the formation of metastable intermediate products.

Now, although the general character of the process may be predicted, no particular statement as to the effects produced in a given system by change of any of the above factors can yet be made, owing to lack of the requisite quantitative data. In this connection it is to be noted that the general application of experimental results which obtain for a given system under given external conditions to another system under similar conditions, or even to the same system under widely differing conditions, is subject to considerable limitation. Conclusions drawn from such extrapolation of experimental evidence will commonly be of little value, and may be altogether misleading; moreover, one may as well guess the final result as arbitrarily choose the data required in calculating it. From this we see that the application of the above simple principles, which determine rock metamorphism, to the complicated rock systems will be no simple matter, but will require extended experimental investigation and a long time. In such investigation the first thing necessary is a definite conception of the general processes of rock metamorphism; this it has been the purpose of the authors to present in the foregoing pages. The choice of particular problems in this large field will doubtless be aided greatly by a study of natural mineral associations from the physical chemical standpoint, a study which at the same time will certainly provide us with information bearing directly on the problems at issue.

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